

UNIVERSITI TEKNOLOGI MARA

**Sr-SITE CATION SUBSTITUTION EFFECTS ON
FORMATION AND SUPERCONDUCTIVITY OF
(Tl,Bi)Sr₂(Ca,Y)Cu₂O₇ CERAMICS**

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Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science

Faculty of Applied Sciences

April 2005

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ABSTRACT

In this work, elemental substitution was employed to stabilize the 1212-phase during the synthesis of $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ superconductors. Although previously this practice was mostly carried out at the Tl and Ca sites, another metallic site i.e. the Sr-site can also be equally important in stabilizing the 1212-phase. Based on the cation substituted at the Sr-site, five series of samples with nominal starting compositions $\text{Tl}_{0.8}\text{Bi}_{0.2}\text{Sr}_{2-w}\text{Cr}_w\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_2\text{O}_7$ ($w = 0 - 0.3$), $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{2-w}\text{Cr}_w\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_2\text{O}_7$ ($w = 0 - 0.5$), $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{2-x}\text{V}_x\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_2\text{O}_7$ ($x = 0 - 0.5$), $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{2-y}\text{Mo}_y\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_2\text{O}_7$ ($y = 0 - 0.5$) and $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_{2-z}\text{In}_z\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_2\text{O}_7$ ($z = 0 - 0.5$) were synthesized and characterized. The polycrystalline samples were prepared by solid state synthesis using the precursor method. The final sintering of the samples was done at around 1000°C for 5 minutes in flowing O_2 . $\text{Tl}_{0.8}\text{Bi}_{0.2}\text{Sr}_2\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_2\text{O}_7$ showed metallic normal state behaviour and was found to superconduct with $T_{c \text{ zero}}$ of 53 K and $T_{c \text{ onset}}$ of 77 K. Initial substitution of Cr for $w = 0.1$ in place of Sr caused $T_{c \text{ zero}}$ to decrease to 46 K. Further substitutions of Cr for $w = 0.2$ and 0.3 produced non-superconducting samples. $\text{Tl}_{0.9}\text{Bi}_{0.1}\text{Sr}_2\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_2\text{O}_7$ also showed metallic normal state behaviour and was found to superconduct at $T_{c \text{ zero}}$ of 60 K and $T_{c \text{ onset}}$ of 100 K. Substitution of $M = \text{Cr}, \text{V}$ and Mo in the $\text{Tl}_{0.9}\text{Bi}_{0.1}(\text{Sr}, M)_2\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_2\text{O}_7$ series produced maximum $T_{c \text{ zero}}$ of 79 K ($w = 0.3$), 82 K ($x = 0.2$) and 84 K ($y = 0.1$), respectively. However, substitution of In was found to suppress T_c . Structurally, all superconducting samples showed 1212 major phase with tetragonal unit cell (space group, $P4/mmm$). XRD analyses, which consistently showed decrease in c -lattice with dopants concentration for all series, suggest successful substitution of the smaller dopants for the larger Sr^{2+} . Generally, the microstructure of the samples changes with the elemental substitutions. Simple valence calculations based on the concept of average Cu valence suggest that the valences of Cr, V and Mo in $\text{Tl}_{0.9}\text{Bi}_{0.1}(\text{Sr}, M)_2\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_2\text{O}_7$ (where $M = \text{Cr}, \text{V}$ and Mo) are 3+ for both Cr and V and 5+ for Mo. Based on changes in normal state behaviour and T_c of all the above series, it is concluded that the Sr-site is significantly important for stability and superconductivity of the $(\text{Tl}, \text{Bi})\text{Sr}_2(\text{Ca}, \text{Y})\text{Cu}_2\text{O}_7$ superconductor.

CHAPTER 1

INTRODUCTION

Superconductors, materials that have no resistance to the flow of electricity, are one of the last great frontiers of scientific discovery. Superconductivity was first observed in mercury by a Dutch physicist H. K. Onnes in 1911. Another characteristic of superconductors, the perfect diamagnetism, was discovered by W. Meissner and R. Ochsenfeld in 1933. These phenomena attracted a lot of attention which led to the introduction of several theories in the attempt of understanding the mechanism of superconductivity. The first well-accepted theory of superconductivity was proposed by Bardeen, Cooper and Schrieffer known as the BCS theory in 1957. Another significant advancement came in 1962 when Brian D. Josephson proposed the tunneling phenomenon, known as the Josephson effect.

A breakthrough in superconductivity was made by K. A. Müller and J. G. Bednorz in 1986 when they reported the superconductivity of lanthanum-barium copper oxide ceramic compound with a T_c of 35 K. This discovery marked the beginning of the era of high temperature superconductivity. Later, YBCO, BSCCO, Tl-based and Hg-based systems were also discovered with significantly higher T_c and better superconducting properties. While these HTS systems showed promising T_c , BSCCO, Tl-based and Hg-based systems have one common problem i.e. phase instability. Fortunately, this problem can be overcome by elemental substitutions. It has been observed that elemental substitution is effective in controlling charge balance in cuprate superconductors, thus stabilize its superconducting phase. Extensive work was dedicated to such processes worldwide not only as a tool to further understand the mechanism of high-temperature superconductivity but also as a means to stabilize materials in which the formal copper valence is considered too high with regards to the ideal formulation.